PATENT ABSTRACTS OF JAPAN

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(54) OPTICAL GLASS AND METHOD FOR MANUFACTURING OPTICAL PRODUCT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide optical glass which has optical characteristics of a high refractive index and low dispersion and low glass transition temperature and which enables long-term stable operation of a heat treatment furnace.

SOLUTION: The optical glass has ≥1.875 refractive index nd, ≥39.5 Abbe's number νd and ≤ 700°C glass transition temperature Tg. In the glass, the proportion (weight ratio) of the total content of La_2O_3, Gd_2O_3, Y_2O_3 and Yb_2O_3 ranges 2 to 4 and the proportion (weight ratio) of the total content of ZrO_2, Ta_2O_5 and Nb_2O_5 ranges 1 to 2 to the total content of SiO_2 and B_2O_3.

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CLAIMS

[Claim(s)]
[Claim 1] Optical glass characterized by for Abbe number nud being [for a refractive index nd] 39.5 or more or more in 1.875, and a glass transition point Tg being 700 degrees C or less.
[Claim 2] At least one sort chosen from La 2O3, Gd2O3, Y2O3, and Yb2O3, It is borosilicate glass containing at least one sort chosen ZrO2, Ta 2O5, and from Nb2O5. Optical glass which the sum total contents of La 2O3, Gd2O3, Y2O3, and Yb2O3 are 2-4 comparatively (weight ratio), and is characterized by being [of the sum total content of ZrO2, Ta 2O5, and Nb2O5] 1-2 comparatively (weight ratio) to the sum total content of SiO2 and B-2 O3.
[Claim 3] Optical glass of a ZnO content [as opposed to the sum total content of SiO2 and B-2 O3 including ZnO] according to claim 2 which 0 is exceeded comparatively (weight ratio) and is two or less.
[Claim 4] The sum total contents of La 2O3, Gd2O3, Y2O3, and Yb2O3 are 2-4 comparatively (weight ratio) to the sum total content of SiO2 and B-2 O3. And optical glass according to claim 3 whose ZnO(s) the sum total contents of ZrO2, Ta 2O5, and Nb2O5 are 1-2 comparatively (weight ratio), and are 0.1-0.5 comparatively (weight ratio).
[Claim 5] A glass presentation is SiO2 at weight %. 3 - 10%, B-2O37-15%, ZnO 0 - 15%, La 2O3 30 - 60%, ZrO2 2 - 8%, and Ta 2O5 13 - 19% is included. And for the sum total content of SiO2 and B-2s O3 and GeO2, the sum total content of 14 - 20% and B-2s O3 and ZnO is [the sum total content of 9% or more and La 2O3, Gd2O3, Y2O3, and Yb2O3] 50 - 60%. Optical glass given in claim 1 to which the sum total content of each above-mentioned component exceeds 95% thru/or any 1 term of 4.
[Claim 6] Li2O Optical glass containing 0 - 1 % of the weight according to claim 5.
[Claim 7] Nb 2O5 Optical glass containing 0 - 3 % of the weight according to claim 5 or 6.
[Claim 8] At weight %, it is B-2 O3. 9 - 12%, and ZnO Optical glass according to claim 5, 6, or 7 whose sum total content of B-2s O3 and ZnO is 12% or more, including 1 - 7%.
[Claim 9] At weight %, it is SiO2. 6 - 9%, B-2 O3 9 - 12%, and GeO2 Optical glass given in claim 5 whose sum total content of SiO2 and B-2s O3 and GeO2 is 16 - 19%, including 0 - 5% thru/or any 1 term of 8.
[Claim 10] A glass presentation is SiO2 at weight %. 3 - 10%, B-2O37-15%, La 2O3 30 - 60%, ZrO2 Optical glass characterized by for the sum total content of SiO2 and B-2 O3 being 14 - 20%, and the sum total content of each above-mentioned component being 95% or more, including 2 - 8%, and 2O513 - 19% of Ta.
[Claim 11] Optical glass according to claim 10 whose glass transition point Tg a part of La 2O3 is permuted by Gd 2O3 and/or Y2O3, 0 - 30 % of the weight and the content of Y2O3 is [the content of Gd 2O3] 0 - 10 % of the weight, and is 700 degrees C or less.
[Claim 12] ZnO Optical glass according to claim 10 or 11 whose sum total content of ZnO and B-2 O3 is 9 % of the weight or more, including 0 - 15 % of the weight.
[Claim 13] Optical glass according to claim 10, 11, or 12 whose glass transition point Tg a part of La 2O3 is permuted by Gd 2O3 and/or Y2O3, the content of 0 - 3 % of the weight and Li2O is [the content

of Gd 2O3 / 0 - 30 % of the weight, and the content of Y2O3 / the content of 0 - 15 % of the weight and Nb 2O5] 0 - 1 % of the weight for the content of 0 - 10 % of the weight, and ZnO, and is 700 degrees C or less.

[Claim 14] (A) The manufacture approach of the optical product characterized by to include the process which carries out press forming of the glass which carried out reheating softening of the glass preforming which comes to preform the glass which dissolved at the process which dissolves the optical glass of a publication in claim 1 thru/or any 1 term of 13, and the (B) above-mentioned (A) process, or this dissolved glass, and the process which carry out the annealing treatment of the glass which fabricated at the (C) above-mentioned (B) process at the temperature near the glass transition point.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Its glass transition point is low while this invention has the optical property of low distribution with a high refractive index in more detail about optical glass, and it is related with the optical glass which a heat treating furnace can long-term stability work.
[0002]
[Description of the Prior Art] Conventionally, in order to bring about a high refractive index and a low distribution property as shown in JP,54-90218,A or JP,54-6042,B, La 2O3, Gd2O3, Y2O3, Ta2O5, ZrO2, etc. contained so much the optical glass which is a high refractive index and has the optical property of low distribution, and since there was little glass network former, such as B-2 O3 and SiO2, it had become what has a strong crystallization inclination extremely. The glass transition point Tg of the high refractive index which the presentation range of the glass which can carry out stable production is restricted, therefore is marketed, and the optical glass of low distribution was over 720 degrees C. The high refractive index indicated by an optical-glass manufacturer's catalog and the property of the optical glass of low distribution are shown in Table 1.
[0003]
[Table 1]

表1

	屈折率 [nd]	アッベ数 [νd]	ガラス転移点 [Tg] (℃)
A	1.88300	40.8	730
B	1.88067	41.01	758
C	1.88300	40.8	738

[0004] Thus, the temperature of viscous flow was very high, for example, the elevated temperature 710 degrees C or more was needed for annealing treatment so that the conventional high refractive index and the optical glass of low distribution might be represented at a glass transition point Tg. Generally the furnace used for the annealing treatment of glass has many which used the stainless steel plate, since the deformation temperature of this ingredient was in about 700 degrees C, when annealing treatment is performed at the temperature exceeding 710 degrees C, this stainless steel plate deforms it and the problem that long-term operation becomes difficult produces it. Moreover, also in manufacture of the lens material by the reheating press etc., the elevated temperature was needed very much, early degradation of a heat treating furnace was brought about, and trouble was caused to stable production. On the other hand, there is a track record which it is stabilized and can be manufactured, without giving

a load special to facility operation, when a glass transition point Tg is glass 700 degrees C or less.
[0005]
[Problem(s) to be Solved by the Invention] While this invention is the basis of such a situation and having the optical property of low distribution with a high refractive index, a glass transition point is low and it aims at offering the manufacture approach of the optical glass which a heat treating furnace can long-term stability work, and the optical product using it.
[0006]
[Means for Solving the Problem] That this invention persons should develop the optical glass which has the aforementioned desirable property The result of having repeated research wholeheartedly about the effect which it has on an optical property, a thermal property, devitrification-proof nature, etc. of each component presentation which constitutes glass, By the sum total content of La 2O3, Gd2O3, Y2O3, and Yb2O3 reaching comparatively, and controlling the rate of the sum total content of ZrO2, Ta 2O5, and Nb2O5 in the specific range to the sum total content of SiO2 and B-2 O3 By having the optical property of low distribution with a high refractive index, and giving a specific process using that the optical glass whose glass transition point is moreover 700 degrees C or less is obtained, and this optical glass Based on a header and this knowledge, it came to complete this invention for a desired optical product being obtained efficiently.
[0007] Namely, the (1) refractive index nd is 1.875 or more, and Abbe number nud of this invention is 39.5 or more. And optical glass characterized by a glass transition point Tg being 700 degrees C or less (optical-glass [of this invention] I is called hereafter.) (2) At least one sort chosen from La 2O3, Gd2O3, Y2O3, and Yb2O3, It is borosilicate glass containing at least one sort chosen ZrO2, Ta 2O5, and from Nb2O5. The sum total contents of La 2O3, Gd2O3, Y2O3, and Yb2O3 are 2-4 comparatively (weight ratio) to the sum total content of SiO2 and B-2 O3. And optical glass characterized by being [of the sum total content of ZrO2, Ta 2O5, and Nb2O5] 1-2 comparatively (weight ratio) (the optical glass II of this invention is called hereafter.)
(3) A glass presentation is SiO2 at weight %. 3 - 10%, B-2 O3 7 - 15%, La 2O3 30 - 60%, ZrO2 2 - 8%, and Ta 2O5 13 - 19% is included. And optical glass characterized by for the sum total content of SiO2 and B-2 O3 being 14 - 20%, and the sum total content of each above-mentioned component being 95% or more (the optical glass III of this invention is called hereafter.) It reaches. [0008] (4) The manufacture approach of the optical product characterized by to include the process which carries out press forming of the glass which carried out reheating softening of the glass preforming which comes to preform the glass which dissolved at the process which dissolves the (A) above-mentioned optical glass I, II, or III, and the (B) above-mentioned (A) process, or this dissolved glass, and the process which carry out the annealing treatment of the glass which fabricated at the (C) above-mentioned (B) process at the temperature near the glass transition point offers
[0009]
[Embodiment of the Invention] The optical glass of this invention has three modes, and the refractive index nd of optical-glass I is [1.875 or more and Abbe number nud] the optical glass with which 39.5 or more and a glass transition point are high refractive-index low distributions of 700 degrees C or less, and have the property of a low glass transition point.
[0010] At least one sort as which optical glass II is chosen from La 2O3, Gd2O3, Y2O3, and Yb2O3, It is borosilicate glass containing at least one sort chosen ZrO2, Ta 2O5, and from Nb2O5. The sum total contents of La 2O3, Gd2O3, Y2O3, and Yb2O3 are 2-4 comparatively (weight ratio) to the sum total content of SiO2 and B-2 O3, and it is the optical glass of the sum total content of ZrO2, Ta 2O5, and Nb2O5 which is 1-2 comparatively (weight ratio).
[0011] On the other hand, a glass presentation is weight % and optical glass III is SiO2. 3 - 10%, B-2 O3 7 - 15%, La 2O3 30 - 60%, ZrO2 2 - 8%, and Ta 2O5 It is the optical glass whose sum total content of each above-mentioned component the sum total content of SiO2 and B-2 O3 is 14 - 20%, including 13 - 19%, and is 95% or more.
[0012] In this optical glass II, the sum total content of SiO2 and B-2 O3 is received. If rate (La2O3+Gd2O3+Y2O3+Yb 2O3)/(SiO2+B-2 O3) of the sum total content of La 2O3, Gd2O3, Y2O3,

and Yb2O3 is lower than 2 at a weight ratio The high refractive index and the high Abbe number which are the purpose of this invention become low, and the content of La 2O3, Gd 2O3, and ZnO that raises distribution compared with Y2O3 is restricted. The optical glass which, as a result, has the glass transition point which can be mass-produced is not obtained, if 4 is exceeded conversely, devitrification-proof nature will become inadequate and the optical glass which can be mass-produced to stability will not be obtained. therefore, the sum total content of SiO2 and B-2 O3 -- receiving -- La2 -- the rate of the sum total content of O3, Gd 2O3 andY2O3, and Yb2O3 is limited to the range of 2-4 by the weight ratio -- having -- desirable -- 3-4 -- it is the range of 3.1-3.7 more preferably.

[0013] On the other hand, to the sum total content of SiO2 and B-2 O3, if rate (ZrO2+Ta2O5+Nb 2O5)/ (SiO2+B-2 O3) of the sum total content of ZrO2, Ta 2O5, and Nb2O5 is lower than 1 at a weight ratio If the optical glass which has the stability which can be mass-produced is not obtained and 2 is conversely exceeded while having the high refractive index made into the purpose of this invention, Abbe number nud will become small and the optical glass of low distribution made into the purpose of this invention will not be obtained. therefore, the rate of the sum total content of ZrO2, Ta 2O5, and Nb2O5 is limited to the range of 1-2 by the weight ratio to the sum total content of SiO2 and B-2 O3 -- having -- desirable -- 1.1-1.5 -- it is the range of 1.2-1.4 more preferably.

[0014] In this optical glass II, ZnO may be included further, content rate ZnO/(SiO2+B-2 O3) of ZnO to the total quantity of SiO2 and B-2 O3 exceeds 0 by the weight ratio, and two or less are desirable, it is one or less exceeding 0 more preferably, and are 0.1-0.5 especially preferably. When the rate of ZnO/ (SiO2+B-2 O3) is in the above-mentioned range, while making glass a high refractive index and low distribution (the wavelength dependency of a refractive index is small), improvement of devitrification-proof nature and the temperature of viscous flow can be reduced.

[0015] As a desirable glass presentation in the optical glass I and II of this invention At weight %, it is SiO2. 3 - 10%, B-2 O3 7 - 15%, GeO2 0 - 5%, 0 - 15% of ZnO(s), La 2O3 30 - 60%, Gd 2O3 0 - 30%, Y2O3 0 - 10%, Yb 2O3 0 - 5%, ZrO2 2 - 8%, and Ta 2O5 13 - 19% is included. And for the sum total content of SiO2 and B-2s O3 and GeO2, the sum total content of 14 - 20% and B-2s O3 and ZnO is [the sum total content of 9% or more and La 2O3, Gd2O3, Y2O3, and Yb2O3] 50 - 60%. That to which the sum total content of each above-mentioned component exceeds 95% can be mentioned.

[0016] In the above-mentioned glass presentation, SiO2 is the indispensable glass network former, in order to maintain devitrification-proof nature, and 3 - 10% of the weight of its range is [the content] desirable. If this content becomes insufficient [less than 3 % of the weight / devitrification-proof nature] and exceeds 10 % of the weight, a refractive index will fall, and the high refractive-index optical glass made into the purpose of this invention is hard to be obtained. When devitrification-proof nature and a refractive index are taken into consideration, this more desirable content of SiO2 is 6.5 - 8.5% of the weight of the range still more preferably six to 9% of the weight.

[0017] B-2 O3 is a component effective for the melting nature of the glass as a mesh formation oxide, and the temperature fall of flow viscosity, and 7 - 15% of the weight of its range is [the content] desirable. If the temperature fall effectiveness of the melting nature of glass or flow viscosity is not fully demonstrated and exceeds 15 % of the weight, a refractive index will fall, and at less than 7 % of the weight, the high refractive-index optical glass made into the purpose of this invention is hard to be obtained. [content / this] When the temperature fall effectiveness and the refractive index of the melting nature of glass or flow viscosity are taken into consideration, the more desirable content of this B-2 O3 is 9.5 - 11% of the weight of the range still more preferably nine to 12% of the weight. GeO2 has the same effectiveness as the above SiO2, and can be made to contain it in 0 - 5% of the weight of the range. If this content exceeds 5 % of the weight, devitrification-proof nature will tend to fall.

[0018] The sum total content of the above SiO2 and B-2s O3 and GeO2 has 14 - 20% of the weight of the desirable range. At less than 14 % of the weight, a crystallization inclination becomes [this sum total content] strong, the optical glass which can be manufactured to stability is hard to be obtained, and if it exceeds 20 % of the weight, the high refractive-index optical glass which a refractive index falls and is made into the purpose of this invention will be hard to be obtained. When a crystallization inclination and a refractive index are taken into consideration, the more desirable sum total content of these SiO2

and B-2s O3 and GeO2 is 16 - 18% of the weight of the range still more preferably 16 to 19% of the weight.
[0019] ZnO has the effectiveness of reducing improvement of devitrification-proof nature, and the temperature of viscous flow while making glass a high refractive index and low distribution (the wavelength dependency of a refractive index is small). Therefore, it is the component which adjusts especially an amount with B-2 O3, and is added suitably. Specifically by adjusting :(SiO2+B-2 O3) ZnO:(La2O3+Gd2O3+Y2O3+Yb 2O3): (Nb2O5+ZrO2+Ta 2O5) While giving the devitrification-proof nature which can make nd 1.875 or more, and can make nud 39.5 or more, and can be manufactured The temperature of viscous flow can be fallen by ****ing more preferably the sum total content of B-2s O3 and ZnO to 12% of the weight or more 9% of the weight or more (it is Tg 700 degrees C or less). As for this ZnO, it is advantageous to make it contain in 0 - 15% of range. When this content exceeds 15 % of the weight, if there is a possibility that devitrification-proof nature may become inadequate when it is going to obtain the refractive index of the range of target, and it is going to maintain the devitrification-proof nature in which stable production is conversely possible, a refractive index will fall, and the optical glass of a high refractive index made into the purpose of this invention is hard to be obtained. The more desirable content of ZnO is 3 - 5% of the weight of the range preferably to 1 - 7% of the weight of the range, and a pan.
[0020] La 2O3 is an indispensable component for obtaining a high refractive index and the optical glass of low distribution, and 30 - 60% of the weight of its range is [the content] desirable. The high refractive index which this content makes the purpose at less than 30 % of the weight, and the optical glass of low distribution are hard to be obtained, if it exceeds 60 % of the weight, devitrification-proof nature will fall and the glass in which stable production is possible will be hard to be obtained. A more desirable content is 40 - 45% of the weight of the range still more preferably 37 to 48% of the weight.
[0021] Gd 2O3 can be made to contain in 0 - 30% of the weight of the range by the permutation with the above La 2O3. If this content exceeds 30 % of the weight, devitrification-proof nature will fall and the glass in which stable production is possible will be hard to be obtained. A more desirable content is 5 - 15% of the weight of the range still more preferably zero to 18% of the weight.
[0022] Y2O3 and Yb2O3 can be made to contain by the permutation with the above La 2O3 in 0 - 10 % of the weight, and 0 - 5% of the weight of the range, respectively. If the content of Y2O3 exceeds 10 % of the weight or the content of Yb 2O3 exceeds 5 % of the weight, devitrification-proof nature will fall and the glass in which stable production is possible will be hard to be obtained. The more desirable content of Y2O3 is 3 - 6% of the weight of the range still more preferably zero to 6% of the weight. Moreover, the more desirable content of Yb 2O3 is 0 - 2% of the weight of the range still more preferably zero to 5% of the weight.
[0023] The above La 2O3, Gd2O3, Y2O3, and Yb2O3 all have effectiveness similar to an optical property, and, as for the sum total content of these components, it is desirable that it is in 50 - 60% of the weight of the range. The high refractive index which this sum total content makes the purpose of this invention at less than 50 % of the weight, and the optical glass of low distribution are hard to be obtained, if it exceeds 60 % of the weight, devitrification-proof nature will fall and optical glass producible to stability will be hard to be obtained. A more desirable sum total content is 54 - 56% of the weight of the range still more preferably 51 to 58% of the weight.
[0024] ZrO2 has the effectiveness of improving devitrification-proof nature by the little addition which brings about a high refractive index and which is a component. The content has 2 - 8% of the weight of the desirable range. At less than 2 % of the weight, if there is a possibility that the optical glass of a high refractive index [content / this] may be hard to be obtained, and the improvement effect of devitrification-proof nature may not fully be demonstrated and it exceeds 8 % of the weight, devitrification-proof nature will fall conversely, a glass transition point becomes high, and there is a possibility that the purpose of this invention may not be reached. A more desirable content is 4 - 6% of the weight of the range still more preferably four to 8% of the weight.
[0025] Ta 2O5 is an indispensable component which brings about a high refractive index, and 13 - 19% of the weight of its range is [the content] desirable. The optical glass of a high refractive index which

this content makes the purpose of this invention at less than 13 % of the weight is hard to be obtained, and if it exceeds 19 % of the weight, while devitrification-proof nature will fall, there is a possibility that the shift by the side of the long wavelength of the transparency absorption end may arise. A more desirable content is 14 - 17% of the weight of the range still more preferably 13 to 17% of the weight.
[0026] As for said each component 2, i.e., SiO, B-2s La [O3, GeO2, ZnO, and] 2O3, Gd2O3, Y2O3, Yb2O3, and the sum total content of ZrO2 and Ta 2O5, in the optical glass I and II of this invention, it is desirable to exceed 95 % of the weight. The optical glass with which this sum total content fills the fall of an optical property and viscous flow temperature made into the purpose of this invention at 95 or less % of the weight and all of devitrification-proof nature is hard to be obtained. A more desirable sum total content is 98 % of the weight or more still more preferably 96% of the weight or more.
[0027] Nb 2O3, WO3 and aluminum 2O3, Bi2O3, Ga2O3, BaO, SrO, CaO and MgO, Na2O, K2O, Li2O, and Sb2O3 can be made to contain by request in the optical glass I and II of this invention in addition to said each component.
[0028] Nb 2O3 and WO3 are components which make devitrification-proof nature improve, and they can be made to contain in 0 - 3% of the weight of the range by little addition, respectively. If the content of Nb 2O3 exceeds 3 % of the weight or the content of WO3 exceeds 3 % of the weight, absorption of the short wavelength region of glass will become strong, and it will become the cause which produces coloring. The more desirable content of Nb 2O3 is 0.5 - 1.5% of the weight of the range still more preferably zero to 1.5% of the weight. Moreover, the more desirable content of WO3 is 0 - 1% of the weight of the range still more preferably zero to 2% of the weight.
[0029] Bi 2O3 is a component which has the effectiveness of reducing Tg by little addition, and can be made to contain in 0 - 3% of the weight of the range. If this content exceeds 3 % of the weight, it will become the cause which produces a fall and coloring of devitrification-proof nature. A more desirable content is 0 - 1% of the weight of the range still more preferably zero to 2% of the weight.
[0030] Although aluminum 2O3 and Ga2O3 may have the operation which improves devitrification-proof nature by little addition, they have the operation which reduces a refractive index to coincidence. Therefore, those contents have 0 - 3% of the weight of the desirable range respectively. The more desirable content of aluminum 2O3 is 0 - 0.5% of the weight of the range still more preferably zero to 2.5% of the weight.
[0031] Although BaO, SrO, CaO, and MgO have the effectiveness of promoting degassing by using a carbonate and a nitrate as raw materials for glass, if the sum total content exceeds 3 % of the weight, devitrification-proof nature will fall and the optical glass in which stable production is possible will be hard to be obtained. Therefore, the sum total content of BaO, SrO, and CaO and MgO has 0 - 3% of the weight of the desirable range. The more desirable content of BaO is 0 - 1% of the weight of the range still more preferably zero to 2% of the weight. Moreover, the more desirable content of SrO is 0 - 1% of the weight of the range still more preferably zero to 2% of the weight.
[0032] Na2O, K2O, and Li2O have effectiveness in the fall of Tg, and the effectiveness of especially Li2O is very high. However, since these components have the large operation which reduces devitrification-proof nature and a refractive index, the sum total content of Na2O, K2O, and Li2O has 0 - 1% of the weight of the desirable range. The more desirable content of Li2O is 0 - 0.5% of the weight of the range.
[0033] Furthermore, Sb 2O3 which is a clarifier can be made to contain in 0 - 1% of the weight of the range. In addition, this Sb 2O3 can also be replaced with other clarifiers 2, for example, SnO etc. The more desirable content of Sb 2O3 is 0 - 0.5% of the weight of the range. A glass presentation is weight % and this invention is SiO2 again. 3 - 10%, B-2 O3 7 - 15%, La 2O3 30 - 60%, ZrO2 2 - 8%, and Ta 2O5 Including 13 - 19%, the sum total content of SiO2 and B-2 O3 is 14 - 20%, and the optical glass III whose sum total content of each above-mentioned component is 95% or more is also offered.
[0034] As this optical glass III, a part of La 2O3 is permuted by Gd 2O3 and/or Y2O3, the content of Gd 2O3 is [0 - 30 % of the weight and the content of Y2O3] 0 - 10 % of the weight, and the optical glass whose glass transition point Tg is 700 degrees C or less is desirable.
[0035] Moreover, it sets to optical glass III and is ZnO. It is desirable that the sum total content of ZnO

and B-2 O3 is 9 % of the weight or more, including 0 - 15 % of the weight. A part of especially La 2O3 is permuted by Gd 2O3 and/or Y2O3, for the content of 0 - 10 % of the weight, and ZnO, the content of 0 - 15 % of the weight and Nb 2O5 is [the content of Gd 2O3 / 0 - 30 % of the weight, and the content of Y2O3 / the content of 0 - 3 % of the weight and Li2O] 0 - 1 % of the weight, and that whose glass transition point Tg is 700 degrees C or less is suitable. The reason for limitation of the range in this optical glass III, the desirable range, etc. are as having explained in said optical glass II.

[0036] According to the manufacture approach of the optical product of this invention, optical products, such as a lens and prism, are obtained by carrying out annealing treatment of the glass which fabricated the optical glass of above-mentioned this invention through the dissolution process and the press-forming process below 700 degrees C depending on the less than temperature near a glass transition point, for example, 720 degrees C, and glass.

[0037] Moreover, optical products, such as a lens and prism, are obtained by making the temperature suitable for press forming (temperature at which viscosity is equivalent to 105-108P), for example, 850 degrees C, reheat and soften glass preforming which preformed the optical glass of this invention through the dissolution process and the forming cycle, and carrying out annealing treatment of the glass which carried out press forming of this below 700 degrees C depending on the less than temperature near a glass transition point, for example, 720 degrees C, and glass.

[0038]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

[0039] Become the glass presentation shown in examples 1-10 and the example 1 of a comparison, and two Table 2 and 3, After often mixing each raw material powder, using a carbonate, a nitrate, a hydroxide, an oxide, etc. as a raw material, it put into the crucible made from platinum, it fused in the furnace set as 1400 degrees C, and it cooled slowly and optical glass was produced, after slushing into the iron frame which carried out the preheating to suitable temperature after churning and founding and holding at the temperature near the Tg for 2 hours.

[0040] In addition, the property of optical glass was measured by the approach shown below. The result is shown in Table 2 and 3.

(1) A refractive index [nd] and the Abbe number [nud]

It measured about the optical glass cooled at the temperature fall rate of 30 degrees C per hour.

(2) It measured under programming-rate the conditions for /of 4 degrees C using the glass transition point Tg apparatus for thermomechanical analysis.

(3) Liquid phase temperature [L. T.]

Glass was put into the 50ml crucible made from platinum, the lid was attached, in the furnace, it held at predetermined temperature for 2 hours, the interior of after [cooling] glass was observed under the 100 times as many microscope as this, and liquid phase temperature was determined from the existence of a crystal. In addition, temperature was changed by 10-degree-C unit.

(4) It asked for the wavelength (nm) of 80% of permeability at the time of measuring spectral transmittance about the polish sample of lambda8010mm thickness.

[0041]

[Table 2]

表2

		実施例			
		1	2	3	4
ガラス組成（重量%）	SiO_2	7.3	7.3	7.3	7.3
	B_2O_3	8.4	9.4	7.6	9.4
	GeO_2	0	0	0	0
	($SiO_2+B_2O_3$)	(15.7)	(16.7)	(14.9)	(16.7)
	($SiO_2+B_2O_3+GeO_2$)	(15.7)	(16.7)	(14.9)	(16.7)
	ZnO	2.2	5.0	11.0	5.0
	(B_2O_3+ZnO)	(10.6)	(14.4)	(18.6)	(14.4)
	La_2O_3	47.8	55.8	41.6	45.8
	Gd_2O_3	10.0	0	10.0	10.0
	Y_2O_3	0	0	0	0
	Yb_2O_3	0	0	0	0
	($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$)	(57.8)	(55.8)	(51.6)	(55.8)
	ZrO_2	5.2	5.2	5.2	7.2
	Ta_2O_5	14.9	15.9	15.9	13.9
	（上記合計）	(95.8)	(98.6)	(98.6)	(98.6)
	Nb_2O_5	0.8	0.8	0.8	1.2
	WO_3	0	0	0	0
	Al_2O_3	2.6	0.4	0.4	0
	Bi_2O_3	0	0	0	0
	BaO	0	0	0	0
	SrO	0	0	0	0
	Li_2O	0.6	0	0	0
	Sb_2O_3	0.2	0.2	0.2	0.2
ZnO／($SiO_2+B_2O_3$)		0.140	0.299	0.738	0.299
($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$) ／ ($SiO_2+B_2O_3$)		3.682	3.341	3.463	3.341
($Nb_2O_5+ZrO_2+Ta_2O_5$) ／ ($SiO_2+B_2O_3$)		1.331	1.311	1.470	1.335
特性	液相温度 [L.T.] (℃)	1290	1280	1290	1260
	屈折率 [nd]	1.88	1.89	1.90	1.89
	アッベ数 [νd]	40.8	40.8	39.6	40.7
	ガラス転移点 [Tg] (℃)	692	699	689	697
	λ80 (nm)	471	450	467	450

[0042]
[Table 3]

表3

		実施例			
		5	6	7	8
ガラス組成（重量%）	SiO_2	6.7	6.7	7.3	8.3
	B_2O_3	10.8	10.8	8.4	9.2
	GeO_2	0	0	0	0
	($SiO_2+B_2O_3$)	(17.5)	(17.5)	(15.7)	(17.5)
	($SiO_2+B_2O_3+GeO_2$)	(17.5)	(17.5)	(15.7)	(17.5)
	ZnO	3.2	4.5	4.5	3.2
	(B_2O_3+ZnO)	(14.0)	(15.3)	(12.9)	(12.4)
	La_2O_3	41.2	41.8	37.8	47.2
	Gd_2O_3	10.0	9.6	18.0	10.0
	Y_2O_3	6.0	3.8	0	0
	Yb_2O_3	0	0	0	0
	($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$)	(57.2)	(55.2)	(55.8)	(57.2)
	ZrO_2	5.2	5.2	5.2	4.2
	Ta_2O_5	15.9	15.9	13.9	16.9
	（上記合計）	(99.0)	(98.3)	(95.1)	(99.0)
	Nb_2O_5	0.8	1.3	0	0.8
	WO_3	0	0	1.8	0
	Al_2O_3	0	0	1.9	0
	Bi_2O_3	0	0	1.0	0
	BaO	0	0	0	0
	SrO	0	0	0	0
	Li_2O	0	0.2	0	0
	Sb_2O_3	0.2	0.2	0.2	0.2
ZnO／($SiO_2+B_2O_3$)		0.183	0.257	0.287	0.183
($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$) ／ ($SiO_2+B_2O_3$)		3.269	3.154	3.554	3.269
($Nb_2O_5+ZrO_2+Ta_2O_5$) ／ ($SiO_2+B_2O_3$)		1.251	1.280	1.217	1.251
特性	液相温度［L.T.］（℃）	1260	1250	1290	1270
	屈折率 ［nd］	1.88	1.88	1.88	1.88
	アッベ数［νd］	41.2	40.9	40.5	41.0
	ガラス転移点［Tg］（℃）	699	672	707	713
	λ80（nm）	443	464	456	450

[0043]
[Table 4]

表4

		実施例		比較例	
		9	10	1	2
ガラス組成（重量%）	SiO_2	5.9	6.7	9.3	9.8
	B_2O_3	12.6	9.7	8.4	14.7
	GeO_2	0	1.5	0.5	0
	($SiO_2+B_2O_3$)	(18.5)	(16.4)	(17.7)	(24.5)
	($SiO_2+B_2O_3+GeO_2$)	(18.5)	(17.9)	(18.2)	(24.5)
	ZnO	0	3.2	0	4.5
	(B_2O_3+ZnO)	(12.6)	(12.9)	(8.4)	(19.2)
	La_2O_3	41.2	42.5	43.8	36.8
	Gd_2O_3	11.0	10.0	14.0	7.6
	Y_2O_3	5.0	4.0	0	3.8
	Yb_2O_3	2.0	0	0	0
	($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$)	(59.2)	(56.5)	(57.8)	(48.2)
	ZrO_2	5.4	5.2	5.2	5.2
	Ta_2O_5	15.9	15.9	13.9	15.9
	（上記合計）	(99.0)	(98.7)	(96.1)	(98.3)
	Nb_2O_5	0.6	0.8	0	1.3
	WO_3	0	0	1.8	0
	Al_2O_3	0	0	1.9	0
	Bi_2O_3	0	0	1.0	0
	BaO	0	0.3	0	0
	SrO	0	0	0	0
	Li_2O	0	0	0	0.2
	Sb_2O_3	0.2	0.2	0.2	0.2
$ZnO/(SiO_2+B_2O_3)$		0	0.195	0	0.184
$(La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3)/(SiO_2+B_2O_3)$		3.200	3.445	3.266	1.967
$(Nb_2O_5+ZrO_2+Ta_2O_5)/(SiO_2+B_2O_3)$		1.184	1.335	1.079	0.914
特性	液相温度 [L.T.] (℃)	1280	1270	1290	1240
	屈折率 [nd]	1.88	1.88	1.88	1.86
	アッベ数 [νd]	41.2	41.1	40.7	42.3
	ガラス転移点 [Tg] (℃)	708	707	735	690
	λ80 (nm)	444	460	460	440

[0044] As shown in the example of Table 2, 3, and 4, while nd is 1.875 or more and nud is 39.5 or more in the glass of this invention, in the examples 1-6, it turns out that Tg is [Tg] 707-713 degrees C or less in 700 degrees C or less and the examples 7-10.

[0045] On the other hand, (Nb2O5+ZrO2+Ta2O5)/(SiO2+B-2 O3) is less than 1.2 in 1.079, and the example 1 of a comparison has Tg as high as 735 degrees C. Moreover, (La2O3+Gd2O3+Y2O3+Yb2O5)/(SiO2+B-2 O3) is less than 3.1 in 1.967, and the example 2 of a comparison has nd as low as 1.86.

[0046] Moreover, the optical glass obtained in the example 6 of this invention was fully softened, as a result of holding for 5 minutes to a 850-degree C electric furnace. On the other hand, in the optical glass obtained in the example 1 of a comparison, softening hardly took place. This shows that a reheating press is possible for the optical glass of this invention at low temperature compared with conventional optical glass.

[0047]

[Effect of the Invention] The optical glass of this invention is the high refractive index and low distribution glass which have the temperature of low viscous flow compared with conventional optical

glass. The annealing treatment and the reheating press in thereby extraordinarily high temperature are less necessary, and producing to stability is possible.

[Translation done.]

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(72)Inventor : TATEWANA KAZUO

(54) OPTICAL GLASS AND METHOD FOR MANUFACTURING OPTICAL PRODUCT

(57)Abstract:
PROBLEM TO BE SOLVED: To provide optical glass which has optical characteristics of a high refractive index and low dispersion and low glass transition temperature and which enables long-term stable operation of a heat treatment furnace.
SOLUTION: The optical glass has ≥1.875 refractive index nd, ≥39.5 Abbe's number νd and ≤ 700° C glass transition temperature Tg. In the glass, the proportion (weight ratio) of the total content of La2O3, Gd2O3, Y2O3 and Yb2O3 ranges 2 to 4 and the proportion (weight ratio) of the total content of ZrO2, Ta2O5 and Nb2O5 ranges 1 to 2 to the total content of SiO2 and B2O3.

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最終頁に続く

(54)【発明の名称】　光学ガラスおよび光学製品の製造方法

(57)【要約】
【課題】　高屈折率で低分散の光学特性を有すると共に、ガラス転移点が低く、熱処理炉の長期安定稼動が可能な光学ガラスを提供する。
【解決手段】　屈折率ｎｄが１．８７５以上で、アッベ数νｄが３９．５以上であり、かつガラス転移点Ｔｇが７００℃以下である光学ガラス、および、SiO_2とB_2O_3との合計含有量に対し、La_2O_3とGd_2O_3とY_2O_3とYb_2O_3との合計含有量の割合（重量比）が２～４であり、かつZrO_2とTa_2O_5とNb_2O_5との合計含有量の割合（重量比）が１～２である光学ガラス。

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【特許請求の範囲】

【請求項１】　屈折率ｎｄが１．８７５以上で、アッベ数ｖｄが３９．５以上であり、ガラス転移点Ｔｇが７００℃以下であることを特徴とする光学ガラス。

【請求項２】　La_2O_3、Gd_2O_3、Y_2O_3およびYb_2O_3の中から選ばれる少なくとも１種と、ZrO_2、Ta_2O_5およびNb_2O_5の中から選ばれる少なくとも１種を含むホウケイ酸ガラスであって、SiO_2とB_2O_3との合計含有量に対し、La_2O_3とGd_2O_3とY_2O_3とYb_2O_3との合計含有量の割合（重量比）が２～４であり、かつZrO_2とTa_2O_5とNb_2O_5との合計含有量の割合（重量比）が１～２であることを特徴とする光学ガラス。

【請求項３】　ＺｎＯを含み、SiO_2とB_2O_3との合計含有量に対するＺｎＯ含有量の割合（重量比）が０を超え２以下である請求項２に記載の光学ガラス。

【請求項４】　SiO_2とB_2O_3との合計含有量に対し、La_2O_3とGd_2O_3とY_2O_3とYb_2O_3との合計含有量の割合（重量比）が２～４であり、かつZrO_2とTa_2O_5とNb_2O_5との合計含有量の割合（重量比）が１～２であり、ＺｎＯの割合（重量比）が０．１～０．５である請求項３に記載の光学ガラス。

【請求項５】　ガラス組成が、重量％で、SiO_2　３～１０％、B_2O_3　７～１５％、ＺｎＯ　０～１５％、La_2O_3　３０～６０％、ZrO_2　２～８％およびTa_2O_5　１３～１９％を含み、かつSiO_2とB_2O_3とGeO_2の合計含有量が１４～２０％、B_2O_3とＺｎＯの合計含有量が９％以上およびLa_2O_3とGd_2O_3とY_2O_3とYb_2O_3の合計含有量が５０～６０％であって、上記各成分の合計含有量が９５％を超える請求項１ないし４のいずれか１項に記載の光学ガラス。

【請求項６】　Li_2O　０～１重量％を含む請求項５に記載の光学ガラス。

【請求項７】　Nb_2O_5　０～３重量％を含む請求項５または６に記載の光学ガラス。

【請求項８】　重量％で、B_2O_3　９～１２％およびＺｎＯ　１～７％を含み、かつB_2O_3とＺｎＯの合計含有量が１２％以上である請求項５、６または７に記載の光学ガラス。

【請求項９】　重量％で、SiO_2　６～９％、B_2O_3　９～１２％およびGeO_2　０～５％を含み、かつSiO_2とB_2O_3とGeO_2の合計含有量が１６～１９％である請求項５ないし８のいずれか１項に記載の光学ガラス。

【請求項１０】　ガラス組成が、重量％で、SiO_2　３～１０％、B_2O_3　７～１５％、La_2O_3　３０～６０％、ZrO_2　２～８％およびTa_2O_5　１３～１９％を含み、かつSiO_2とB_2O_3の合計含有量が１４～２０％であって、上記各成分の合計含有量が９５％以上であることを特徴とする光学ガラス。

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【請求項１１】　La_2O_3の一部がGd_2O_3および／またはY_2O_3で置換され、Gd_2O_3の含有量が０～３０重量％およびY_2O_3の含有量が０～１０重量％であり、ガラス転移点Ｔｇが７００℃以下である請求項１０に記載の光学ガラス。

【請求項１２】　ＺｎＯ　０～１５重量％を含み、かつＺｎＯとB_2O_3との合計含有量が９重量％以上である請求項１０または１１に記載の光学ガラス。

【請求項１３】　La_2O_3の一部がGd_2O_3および／またはY_2O_3で置換され、Gd_2O_3の含有量が０～３０重量％、Y_2O_3の含有量が０～１０重量％、ＺｎＯの含有量が０～１５重量％、Nb_2O_5の含有量が０～３重量％およびLi_2Oの含有量が０～１重量％であり、ガラス転移点Ｔｇが７００℃以下である請求項１０、１１または１２に記載の光学ガラス。

【請求項１４】　（Ａ）請求項１ないし１３のいずれか１項に記載の光学ガラスを溶解する工程、

（Ｂ）上記（Ａ）工程で溶解したガラスまたは該溶解したガラスを予備成形してなるガラスプリフォームを再加熱軟化したガラスをプレス成形する工程、および

（Ｃ）上記（Ｂ）工程で成形したガラスをガラス転移点近傍の温度でアニール処理する工程、を含むことを特徴とする光学製品の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は光学ガラスに関し、さらに詳しくは、高屈折率で低分散の光学特性を有すると共に、ガラス転移点が低く、熱処理炉の長期安定稼動が可能な光学ガラスに関するものである。

【０００２】

【従来の技術】従来、高屈折率で、かつ低分散の光学特性を有する光学ガラスは、例えば特開昭５４－９０２１８号公報や特公昭５４－６０４２号公報に示されているように、高屈折率、低分散特性をもたらすために、La_2O_3、Gd_2O_3、Y_2O_3、Ta_2O_5、ZrO_2などが多量に含有され、B_2O_3やSiO_2などのガラス網目形成成分が少ないために、極めて結晶化傾向が強いものになっていた。安定生産できるガラスの組成範囲は限られており、したがって、市販されている高屈折率、低分散の光学ガラスのガラス転移点Ｔｇは７２０℃を超えていた。表１に、光学ガラスメーカーのカタログに記載されている高屈折率、低分散の光学ガラスの特性を示す。

【０００３】

【表１】

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表１

	屈折率 [nd]	アッベ数 [νd]	ガラス転移点 [Tg] (℃)
A	1.88300	40.8	730
B	1.88067	41.01	758
C	1.88300	40.8	738

【０００４】このように、従来の高屈折率、低分散の光学ガラスは、ガラス転移点Ｔｇに代表されるように粘性流動の温度が極めて高く、例えばアニール処理には７１０℃以上の高温を必要としていた。一般に、ガラスのアニール処理に用いる炉は、ステンレス鋼板を使用したものが多く、この材料の変形温度は７００℃近傍にあることから、アニール処理を７１０℃を上回る温度で行った場合、該ステンレス鋼板が変形し、長期的な稼動が困難となるという問題が生じる。また、再加熱プレスによるレンズ素材などの製造においても非常に高温を必要とし、熱処理炉の早期劣化をもたらし、安定生産に支障をきたしていた。一方、ガラス転移点Ｔｇが７００℃以下のガラスの場合、設備稼動に特別の負荷を与えることなく、安定して製造し得る実績がある。

【０００５】

【発明が解決しようとする課題】本発明は、このような事情のもとで、高屈折率で低分散の光学特性を有すると共に、ガラス転移点が低く、熱処理炉の長期安定稼動が可能な光学ガラス、およびそれを用いた光学製品の製造方法を提供することを目的とするものである。

【０００６】

【課題を解決するための手段】本発明者らは、前記の好ましい特性を有する光学ガラスを開発すべく、ガラスを構成する各成分組成の光学的特性、熱的特性および耐失透性などに与える影響について鋭意研究を重ねた結果、SiO_2とB_2O_3との合計含有量に対し、La_2O_3とGd_2O_3とY_2O_3とYb_2O_3との合計含有量の割合およびZrO_2とTa_2O_5とNb_2O_5との合計含有量の割合を特定範囲に制御することにより、高屈折率で低分散の光学特性を有し、しかもガラス転移点が７００℃以下である光学ガラスが得られること、そして、この光学ガラスを用い、特定の工程を施すことにより、所望の光学製品が効率よく得られることを見出し、この知見に基づいて本発明を完成するに至った。

【０００７】すなわち、本発明は、（１）屈折率ｎｄが１．８７５以上で、アッベ数νｄが３９．５以上であり、かつガラス転移点Ｔｇが７００℃以下であることを特徴とする光学ガラス（以下、本発明の光学ガラスＩと称する。）、（２）La_2O_3、Gd_2O_3、Y_2O_3およびYb_2O_3の中から選ばれる少なくとも１種と、ZrO_2、Ta_2O_5およびNb_2O_5の中から選ばれる少なくとも１種を含むホウケイ酸ガラスであって、SiO_2とB_2O_3との合計含有量に対し、La_2O_3とGd_2O_3とY_2O_3とYb_2O_3との合計含有量の割合（重量比）が２～４であり、かつZrO_2とTa_2O_5とNb_2O_5との合計含有量の割合（重量比）が１～２であることを特徴とする光学ガラス（以下、本発明の光学ガラスIIと称する。）

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（３）ガラス組成が、重量％で、SiO_2　３～１０％、B_2O_3　７～１５％、La_2O_3　３０～６０％、ZrO_2　２～８％およびTa_2O_5　１３～１９％を含み、かつSiO_2とB_2O_3の合計含有量が１４～２０％であって、上記各成分の合計含有量が９５％以上であることを特徴とする光学ガラス（以下、本発明の光学ガラスIIIと称する。）、および

【０００８】（４）（Ａ）上記光学ガラスＩ、IIまたはIIIを溶解する工程、（Ｂ）上記（Ａ）工程で溶解したガラスまたは該溶解したガラスを予備成形してなるガラスプリフォームを再加熱軟化したガラスをプレス成形する工程、および（Ｃ）上記（Ｂ）工程で成形したガラスをガラス転移点近傍の温度でアニール処理する工程、を含むことを特徴とする光学製品の製造方法、を提供するものである。

【０００９】

【発明の実施の形態】本発明の光学ガラスは３つの態様があり、光学ガラスＩは、屈折率ｎｄが１．８７５以上、アッベ数νｄが３９．５以上、ガラス転移点が７００℃以下の高屈折率低分散で、かつ低ガラス転移点の特性を有する光学ガラスである。

【００１０】光学ガラスIIは、La_2O_3、Gd_2O_3、Y_2O_3およびYb_2O_3の中から選ばれる少なくとも１種と、ZrO_2、Ta_2O_5およびNb_2O_5の中から選ばれる少なくとも１種を含むホウケイ酸ガラスであって、SiO_2とB_2O_3との合計含有量に対し、La_2O_3とGd_2O_3とY_2O_3とYb_2O_3との合計含有量の割合（重量比）が２～４であり、かつZrO_2とTa_2O_5とNb_2O_5との合計含有量の割合（重量比）が１～２である光学ガラスである。

【００１１】一方、光学ガラスIIIは、ガラス組成が、重量％で、SiO_2　３～１０％、B_2O_3　７～１５％、La_2O_3　３０～６０％、ZrO_2　２～８％およびTa_2O_5　１３～１９％を含み、かつSiO_2とB_2O_3の合計含有量が１４～２０％であって、上記各成分の合計含有量が９５％以上である光学ガラスである。

【００１２】該光学ガラスIIにおいて、SiO_2とB_2O_3との合計含有量に対し、La_2O_3とGd_2O_3とY_2O_3とYb_2O_3との合計含有量の割合（$La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$）／（$SiO_2+B_2O_3$）が、重量比で２より低いと、本発明の目的である高屈折率および高アッベ数が低くなり、La_2O_3やGd_2O_3、Y_2O_3に

比べて分散を高めるＺｎＯの含有量が制限され、その結果量産可能なガラス転移点を有する光学ガラスが得られないし、逆に４を超えると耐失透性が不十分になり、安定に量産可能な光学ガラスが得られない。したがって、SiO_2とB_2O_3との合計含有量に対し、La_2O_3とGd_2O_3とY_2O_3とYb_2O_3との合計含有量の割合は、重量比で２～４の範囲に限定され、好ましくは３～４、より好ましくは３．１～３．７の範囲である。

【００１３】一方、SiO_2とB_2O_3との合計含有量に対し、ZrO_2とTa_2O_5とNb_2O_5との合計含有量の割合（$ZrO_2+Ta_2O_5+Nb_2O_5$）／（$SiO_2+B_2O_3$）が、重量比で１より低いと、本発明の目的とする高屈折率を有すると共に、量産可能な安定性を有する光学ガラスが得られないし、逆に２を超えると、アッベ数νdが小さくなり、本発明の目的とする低分散の光学ガラスが得られない。したがって、SiO_2とB_2O_3との合計含有量に対し、ZrO_2とTa_2O_5とNb_2O_5との合計含有量の割合は、重量比で１～２の範囲に限定され、好ましくは１．１～１．５、より好ましくは１．２～１．４の範囲である。

【００１４】この光学ガラスIIにおいては、さらにＺｎＯを含んでいてもよく、SiO_2とB_2O_3との合計量に対するＺｎＯの含有割合ＺｎＯ／（$SiO_2+B_2O_3$）は、重量比で０を超え２以下が好ましく、より好ましくは０を超えて１以下であり、特に好ましくは０．１～０．５である。ＺｎＯ／（$SiO_2+B_2O_3$）の割合が上記範囲にあることにより、ガラスを高屈折率および低分散（屈折率の波長依存性が小さい）にすると共に、耐失透性の良化および粘性流動の温度を低下させることができる。

【００１５】本発明の光学ガラスIおよびIIにおける好ましいガラス組成としては、重量％で、SiO_2　３～１０％、B_2O_3　７～１５％、GeO_2　０～５％、ＺｎＯ０～１５％、La_2O_3　３０～６０％、Gd_2O_3　０～３０％、Y_2O_3　０～１０％、Yb_2O_3　０～５％、ZrO_2　２～８％およびTa_2O_5　１３～１９％を含み、かつSiO_2とB_2O_3とGeO_2の合計含有量が１４～２０％、B_2O_3とＺｎＯの合計含有量が９％以上およびLa_2O_3とGd_2O_3とY_2O_3とYb_2O_3の合計含有量が５０～６０％であって、上記各成分の合計含有量が９５％を超えるものを挙げることができる。

【００１６】上記ガラス組成において、SiO_2は耐失透性を維持するために必須のガラス網目形成成分であって、その含有量は３～１０重量％の範囲が好ましい。この含有量が３重量％未満では耐失透性が不十分となるし、１０重量％を超えると屈折率が低下し、本発明の目的とする高屈折率光学ガラスが得られにくい。耐失透性および屈折率を考慮すると、このSiO_2のより好ましい含有量は６～９重量％、さらに好ましくは６．５～８．５重量％の範囲である。

【００１７】B_2O_3は網目形成酸化物として、あるいはガラスの溶融性、流動粘性の温度低下に効果的な成分であって、その含有量は７～１５重量％の範囲が好ましい。この含有量が７重量％未満ではガラスの溶融性や流動粘性の温度低下効果が十分に発揮されないし、１５重量％を超えると屈折率が低下し、本発明の目的とする高屈折率光学ガラスが得られにくい。ガラスの溶融性や流動粘性の温度低下効果および屈折率を考慮すると、このB_2O_3のより好ましい含有量は９～１２重量％、さらに好ましくは９．５～１１重量％の範囲である。GeO_2は上記SiO_2と同様の効果を有し、０～５重量％の範囲で含有させることができる。この含有量が５重量％を超えると耐失透性が低下しやすい。

【００１８】上記SiO_2とB_2O_3とGeO_2の合計含有量は１４～２０重量％の範囲が好ましい。この合計含有量が１４重量％未満では結晶化傾向が強くなり安定に製造可能な光学ガラスが得られにくいし、２０重量％を超えると屈折率が低下して本発明の目的とする高屈折率光学ガラスが得られにくい。結晶化傾向および屈折率を考慮すると、このSiO_2とB_2O_3とGeO_2のより好ましい合計含有量は１６～１９重量％、さらに好ましくは１６～１８重量％の範囲である。

【００１９】ＺｎＯはガラスを高屈折率および低分散（屈折率の波長依存性が小さい）にすると共に、耐失透性の良化および粘性流動の温度を低下させる効果を有する。したがって、特にB_2O_3との量の調整を行い適宜添加する成分である。具体的には、（$SiO_2+B_2O_3$）：ＺｎＯ：（$La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$）：（$Nb_2O_5+ZrO_2+Ta_2O_5$）を調整することにより、ndを１．８７５以上、νdを３９．５以上とし、かつ製造可能な耐失透性をもたせると共に、B_2O_3とＺｎＯの合計含有量を、好ましくは９重量％以上、より好ましくは１２重量％以上にすることで、粘性流動の温度を低下（Ｔｇを７００℃以下）することができる。このＺｎＯは０～１５％の範囲で含有させるのが有利である。この含有量が１５重量％を超える場合、目的の範囲の屈折率を得ようとすると耐失透性が不十分になるおそれがあるし、逆に安定生産可能な耐失透性を維持しようとすると屈折率が低下し、本発明の目的とする高屈折率の光学ガラスが得られにくい。より好ましいＺｎＯの含有量は１～７重量％の範囲、さらに好ましくは３～５重量％の範囲である。

【００２０】La_2O_3は高屈折率、低分散の光学ガラスを得るための必須の成分であって、その含有量は３０～６０重量％の範囲が好ましい。この含有量が３０重量％未満では目的とする高屈折率、低分散の光学ガラスが得られにくいし、６０重量％を超えると耐失透性が低下し、安定生産可能なガラスが得られにくい。より好ましい含有量は３７～４８重量％、さらに好ましくは４０～４５重量％の範囲である。

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【００２１】Gd_2O_3は上記La_2O_3との置換により０～３０重量％の範囲で含有させることができる。この含有量が３０重量％を超えると耐失透性が低下し、安定生産可能なガラスが得られにくい。より好ましい含有量は０～１８重量％、さらに好ましくは５～１５重量％の範囲である。

【００２２】Y_2O_3およびYb_2O_3もまた、上記La_2O_3との置換により、それぞれ０～１０重量％および０～５重量％の範囲で含有させることができる。Y_2O_3の含有量が１０重量％を超えたり、Yb_2O_3の含有量が５重量％を超えると耐失透性が低下し、安定生産可能なガラスが得られにくい。Y_2O_3のより好ましい含有量は０～６重量％、さらに好ましくは３～６重量％の範囲である。また、Yb_2O_3のより好ましい含有量は０～５重量％、さらに好ましくは０～２重量％の範囲である。

【００２３】上記La_2O_3とGd_2O_3、Y_2O_3およびYb_2O_3は、いずれも光学特性に対しては、類似する効果を有しており、これらの成分の合計含有量は５０～６０重量％の範囲にあるのが好ましい。この合計含有量が５０重量％未満では本発明の目的とする高屈折率、低分散の光学ガラスが得られにくいし、６０重量％を超えると耐失透性が低下して、安定に生産可能な光学ガラスが得られにくい。より好ましい合計含有量は５１～５８重量％、さらに好ましくは５４～５６重量％の範囲である。

【００２４】ZrO_2は高屈折率をもたらす成分であり、かつ少量の添加で耐失透性を改善する効果を有している。その含有量は２～８重量％の範囲が好ましい。この含有量が２重量％未満では高屈折率の光学ガラスが得られにくく、かつ耐失透性の改善効果が十分に発揮されないおそれがあるし、８重量％を超えると逆に耐失透性が低下し、ガラス転移点が高くなり、本発明の目的が達せられないおそれがある。より好ましい含有量は４～８重量％、さらに好ましくは４～６重量％の範囲である。

【００２５】Ta_2O_5は高屈折率をもたらす必須成分であり、その含有量は１３～１９重量％の範囲が好ましい。この含有量が１３重量％未満では本発明の目的とする高屈折率の光学ガラスが得られにくいし、１９重量％を超えると耐失透性が低下すると共に、透過吸収端の長波長側へのシフトが生じるおそれがある。より好ましい含有量は１３～１７重量％、さらに好ましくは１４～１７重量％の範囲である。

【００２６】本発明の光学ガラスＩおよびＩＩにおいては、前記各成分、すなわち、SiO_2、B_2O_3、GeO_2、ZnO、La_2O_3、Gd_2O_3、Y_2O_3、Yb_2O_3、ZrO_2およびTa_2O_5の合計含有量は、９５重量％を超えることが好ましい。この合計含有量が９５重量％以下では、本発明の目的とする光学特性、粘性流動温度の低下および耐失透性のいずれをも満たす光学ガラスが得られにくい。より好ましい合計含有量は９６重量％以上、さらに好ましくは９８重量％以上である。

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【００２７】本発明の光学ガラスＩおよびＩＩにおいて、前記各成分以外に、Nb_2O_3、WO_3、Al_2O_3、Bi_2O_3、Ga_2O_3、BaO、SrO、CaO、MgO、Na_2O、K_2O、Li_2OおよびSb_2O_3を所望により含有させることができる。

【００２８】Nb_2O_3およびWO_3は少量の添加によって、耐失透性を良化させる成分であり、それぞれ０～３重量％の範囲で含有させることができる。Nb_2O_3の含有量が３重量％を超えたり、WO_3の含有量が３重量％を超えると、ガラスの短波長域の吸収が強まり、着色を生じる原因となる。Nb_2O_3のより好ましい含有量は０～１．５重量％、さらに好ましくは０．５～１．５重量％の範囲である。また、WO_3のより好ましい含有量は０～２重量％、さらに好ましくは０～１重量％の範囲である。

【００２９】Bi_2O_3は少量の添加でＴｇを低下させる効果を有する成分であり、０～３重量％の範囲で含有させることができる。この含有量が３重量％を超えると耐失透性の低下や着色を生じる原因となる。より好ましい含有量は０～２重量％、さらに好ましくは０～１重量％の範囲である。

【００３０】Al_2O_3およびGa_2O_3は少量の添加で耐失透性を改善する作用を有する場合があるが、同時に屈折率を低下させる作用を有している。したがって、それらの含有量は、それぞれ０～３重量％の範囲が好ましい。Al_2O_3のより好ましい含有量は０～２．５重量％、さらに好ましくは０～０．５重量％の範囲である。

【００３１】BaO、SrO、CaOおよびMgOは、ガラス原料として炭酸塩や硝酸塩を用いることにより脱泡を促進させる効果を有しているが、その合計含有量が３重量％を超えると耐失透性が低下して、安定生産可能な光学ガラスが得られにくい。したがって、BaOとSrOとCaOとMgOの合計含有量は０～３重量％の範囲が好ましい。BaOのより好ましい含有量は０～２重量％、さらに好ましくは０～１重量％の範囲である。また、SrOのより好ましい含有量は０～２重量％、さらに好ましくは０～１重量％の範囲である。

【００３２】Na_2O、K_2OおよびLi_2Oは、Ｔｇの低下に効果を有し、特にLi_2Oはその効果が極めて高い。しかしながら、これらの成分は耐失透性および屈折率を低下させる作用が大きいため、Na_2OとK_2OとLi_2Oの合計含有量は０～１重量％の範囲が好ましい。Li_2Oのより好ましい含有量は０～０．５重量％の範囲である。

【００３３】さらに、清澄剤であるSb_2O_3を０～１重量％の範囲で含有させることができる。なお、このSb_2O_3は、他の清澄剤、例えばSnO_2などと置き換えることもできる。Sb_2O_3のより好ましい含有量は０～０．５重量％の範囲である。本発明はまた、ガラス組成が、重量％で、SiO_2　３～１０％、B_2O_3　７～１

５%、La_2O_3　３０～６０%、ZrO_2　２～８%およびTa_2O_5　１３～１９%を含み、かつSiO_2とB_2O_3の合計含有量が１４～２０%であって、上記各成分の合計含有量が９５%以上である光学ガラスIIIをも提供する。

【００３４】この光学ガラスIIIとしては、La_2O_3の一部がGd_2O_3および／またはY_2O_3で置換され、Gd_2O_3の含有量が０～３０重量%およびY_2O_3の含有量が０～１０重量%であり、ガラス転移点Ｔｇが７００℃以下である光学ガラスが好ましい。

【００３５】また、光学ガラスIIIにおいては、ＺｎＯ　０～１５重量%を含み、かつＺｎＯとB_2O_3との合計含有量が９重量%以上であるのが好ましい。特にLa_2O_3の一部がGd_2O_3および／またはY_2O_3で置換され、Gd_2O_3の含有量が０～３０重量%、Y_2O_3の含有量が０～１０重量%、ＺｎＯの含有量が０～１５重量%、Nb_2O_5の含有量が０～３重量%およびLi_2Oの含有量が０～１重量%であり、ガラス転移点Ｔｇが７００℃以下であるものが好適である。該光学ガラスIIIにおける範囲の限定理由及び好ましい範囲などは、前記光学ガラスIIにおいて説明したとおりである。

【００３６】本発明の光学製品の製造方法によれば、前述の本発明の光学ガラスを溶解工程、プレス成形工程を経て成形したガラスを、ガラス転移点付近の温度、例えば７２０℃以下、ガラスによっては７００℃以下でアニール処理することにより、レンズ、プリズムなどの光学製品が得られる。

【００３７】また、本発明の光学ガラスを溶解工程、成形工程を経て予備成形したガラスプリフォームを、プレス成形に適した温度（粘度が10^5～10^8ポアズに相当する温度）、例えば８５０℃に再加熱して軟化させ、これをプレス成形したガラスを、ガラス転移点付近の温度、例えば７２０℃以下、ガラスによっては７００℃以下でアニール処理することにより、レンズ、プリズムなどの光学製品が得られる。

【００３８】

【実施例】次に、本発明を実施例により、さらに詳細に説明するが、本発明は、これらの例によってなんら限定されるものではない。

【００３９】実施例１～１０および比較例１、２

表２および表３に示すガラス組成になるように、原料として炭酸塩、硝酸塩、水酸化物、酸化物などを用い、各原料粉末をよく混合したのち、白金製坩堝に入れ、１４００℃に設定された炉内で溶融し、撹拌、清澄後適当な温度に予熱した鉄製枠に流し込み、Ｔｇ近傍の温度で２時間保持したのち、徐冷して光学ガラスを作製した。

【００４０】なお、光学ガラスの特性は、以下に示す方法により測定した。その結果を表２および表３に示す。

（１）屈折率［ｎｄ］およびアッベ数［νｄ］

１時間当たり、３０℃の降温速度で冷却した光学ガラスについて測定した。

（２）ガラス転移点Ｔｇ

熱機械分析装置を用いて、昇温速度４℃／分の条件下で測定した。

（３）液相温度［Ｌ．Ｔ．］

５０ミリリットルの白金製坩堝にガラスを入れ、蓋を付けて炉内に所定の温度で２時間保持し、冷却後ガラス内部を１００倍の顕微鏡で観察し、結晶の有無から、液相温度を決定した。なお、温度は１０℃刻みで変化させた。

（４）λ８０

１０ｍｍ厚の研磨サンプルについて、分光透過率を測定した際の透過率８０%の波長（ｎｍ）を求めた。

【００４１】

【表２】

表２

		実施例			
		1	2	3	4
ガラス組成（重量%）	SiO_2	7.3	7.3	7.3	7.3
	B_2O_3	8.4	9.4	7.6	9.4
	GeO_2	0	0	0	0
	($SiO_2+B_2O_3$)	(15.7)	(16.7)	(14.9)	(16.7)
	($SiO_2+B_2O_3+GeO_2$)	(15.7)	(16.7)	(14.9)	(16.7)
	ZnO	2.2	5.0	11.0	5.0
	(B_2O_3+ZnO)	(10.6)	(14.4)	(18.6)	(14.4)
	La_2O_3	47.8	55.8	41.6	45.8
	Gd_2O_3	10.0	0	10.0	10.0
	Y_2O_3	0	0	0	0
	Yb_2O_3	0	0	0	0
	($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$)	(57.8)	(55.8)	(51.6)	(55.8)
	ZrO_2	5.2	5.2	5.2	7.2
	Ta_2O_5	14.9	15.9	15.9	13.9
	（上記合計）	(95.8)	(98.6)	(98.6)	(98.6)
	Nb_2O_5	0.8	0.8	0.8	1.2
	WO_3	0	0	0	0
	Al_2O_3	2.6	0.4	0.4	0
	Bi_2O_3	0	0	0	0
	BaO	0	0	0	0
	SrO	0	0	0	0
	Li_2O	0.6	0	0	0
	Sb_2O_3	0.2	0.2	0.2	0.2
ZnO／($SiO_2+B_2O_3$)		0.140	0.299	0.738	0.299
($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$)／($SiO_2+B_2O_3$)		3.682	3.341	3.463	3.341
($Nb_2O_5+ZrO_2+Ta_2O_5$)／($SiO_2+B_2O_3$)		1.331	1.311	1.470	1.335
特性	液相温度 [L.T.] (℃)	1290	1280	1290	1260
	屈折率 [nd]	1.88	1.89	1.90	1.89
	アッベ数 [νd]	40.8	40.8	39.6	40.7
	ガラス転移点 [Tg] (℃)	692	699	689	697
	λ80 (nm)	471	450	467	450

【００４２】　　【表３】

表３

		実施例			
		5	6	7	8
ガラス組成（重量%）	SiO_2	6.7	6.7	7.3	8.3
	B_2O_3	10.8	10.8	8.4	9.2
	GeO_2	0	0	0	0
	($SiO_2+B_2O_3$)	(17.5)	(17.5)	(15.7)	(17.5)
	($SiO_2+B_2O_3+GeO_2$)	(17.5)	(17.5)	(15.7)	(17.5)
	ZnO	3.2	4.5	4.5	3.2
	(B_2O_3+ZnO)	(14.0)	(15.3)	(12.9)	(12.4)
	La_2O_3	41.2	41.8	37.8	47.2
	Gd_2O_3	10.0	9.6	18.0	10.0
	Y_2O_3	6.0	3.8	0	0
	Yb_2O_3	0	0	0	0
	($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$)	(57.2)	(55.2)	(55.8)	(57.2)
	ZrO_2	5.2	5.2	5.2	4.2
	Ta_2O_5	15.9	15.9	13.9	16.9
	（上記合計）	(99.0)	(98.3)	(95.1)	(99.0)
	Nb_2O_5	0.8	1.3	0	0.8
	WO_3	0	0	1.8	0
	Al_2O_3	0	0	1.9	0
	Bi_2O_3	0	0	1.0	0
	BaO	0	0	0	0
	SrO	0	0	0	0
	Li_2O	0	0.2	0	0
	Sb_2O_3	0.2	0.2	0.2	0.2
$ZnO/(SiO_2+B_2O_3)$		0.183	0.257	0.287	0.183
$(La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3)/(SiO_2+B_2O_3)$		3.269	3.154	3.554	3.269
$(Nb_2O_5+ZrO_2+Ta_2O_5)/(SiO_2+B_2O_3)$		1.251	1.280	1.217	1.251
特性	液相温度［L.T.］ (℃)	1260	1250	1290	1270
	屈折率 ［nd］	1.88	1.88	1.88	1.88
	アッベ数［νd］	41.2	40.9	40.5	41.0
	ガラス転移点［Tg］ (℃)	699	672	707	713
	λ80 (nm)	443	464	456	450

【００４３】　　【表４】

表４

		実施例		比較例	
		9	10	1	2
ガラス組成（重量%）	SiO_2	5.9	6.7	9.3	9.8
	B_2O_3	12.6	9.7	8.4	14.7
	GeO_2	0	1.5	0.5	0
	($SiO_2+B_2O_3$)	(18.5)	(16.4)	(17.7)	(24.5)
	($SiO_2+B_2O_3+GeO_2$)	(18.5)	(17.9)	(18.2)	(24.5)
	ZnO	0	3.2	0	4.5
	(B_2O_3+ZnO)	(12.6)	(12.9)	(8.4)	(19.2)
	La_2O_3	41.2	42.5	43.8	36.8
	Gd_2O_3	11.0	10.0	14.0	7.6
	Y_2O_3	5.0	4.0	0	3.8
	Yb_2O_3	2.0	0	0	0
	($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$)	(59.2)	(56.5)	(57.8)	(48.2)
	ZrO_2	5.4	5.2	5.2	5.2
	Ta_2O_5	15.9	15.9	13.9	15.9
	（上記合計）	(99.0)	(98.7)	(96.1)	(98.3)
	Nb_2O_5	0.6	0.8	0	1.3
	WO_3	0	0	1.8	0
	Al_2O_3	0	0	1.9	0
	Bi_2O_3	0	0	1.0	0
	BaO	0	0.3	0	0
	SrO	0	0	0	0
	Li_2O	0	0	0	0.2
	Sb_2O_3	0.2	0.2	0.2	0.2
ZnO／($SiO_2+B_2O_3$)		0	0.195	0	0.184
($La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_3$)／($SiO_2+B_2O_3$)		3.200	3.445	3.266	1.967
($Nb_2O_5+ZrO_2+Ta_2O_5$)／($SiO_2+B_2O_3$)		1.184	1.335	1.079	0.914
特性	液相温度 [L.T.] (℃)	1280	1270	1290	1240
	屈折率 [nd]	1.88	1.88	1.88	1.86
	アッベ数 [νd]	41.2	41.1	40.7	42.3
	ガラス転移点 [Tg] (℃)	708	707	735	690
	λ80 (nm)	444	460	460	440

【００４４】表２、表３および表４の実施例に示すように、本発明のガラスにおいては、ｎｄが１．８７５以上で、νｄが３９．５以上であると共に、実施例１～６ではＴｇが７００℃以下、実施例７～１０ではＴｇが７０７～７１３℃以下であることが分かる。

【００４５】一方、比較例１は、（$Nb_2O_5+ZrO_2+Ta_2O_5$）／（$SiO_2+B_2O_3$）が１．０７９で１．２未満であり、Ｔｇが７３５℃と高い。また、比較例２は、（$La_2O_3+Gd_2O_3+Y_2O_3+Yb_2O_5$）／（$SiO_2+B_2O_3$）が１．９６７で３．１未満であり、ｎｄが１．８６と低い。

【００４６】また、本発明の実施例６で得られた光学ガラスを、８５０℃の電気炉に５分間保持した結果、十分に軟化した。一方、比較例１で得られた光学ガラスではほとんど軟化が起こらなかった。このことは、本発明の光学ガラスは、従来の光学ガラスに比べて低温で再加熱プレスが可能なことを示している。

【００４７】

【発明の効果】本発明の光学ガラスは、従来の光学ガラスに比べて、低い粘性流動の温度を有する高屈折率、低分散ガラスである。これにより、特別高い温度におけるアニール処理や再加熱プレスが必要でなくなり、安定に生産することが可能である。

フロントページの続き

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